CHAPTER # 14 D and F block elements

→ Inner transition elements

Transition element

G. electronic configuration: $(n-1)d^{1-10}\ ns^{1-2}$ • Outer transition elements

Defination
outermost d and f is incomplete in atomic and ionic state

Position
They are located b/w s and p block their properties are in b/w s and p block

Example
$Fe_{26} = 1s^2 2s^2 2p^6 3s^2 \ldots 4s^2 3d^6$

• d-orbital in complete

Series of transition elements

① 3d - first outer transition series
Sc → Zn (sari wali car mein leco nahi (Zn))
(21) (30)

② 4d second outer transition series
Y39 → Cd(48)

③ 5d third outer transition series
La57 → Hg 80

④ 6d fourth outer transition series
Ac(89) → onward

F-block series
① 4f First inner transition series
Ce58 → Lu71
② 5f second inner transition series
Th(90) → Lr(103)

Coinage metals
Cu Ag Au

Cu → $4s^1 3d^{10}$ half filled, partially filled

• ionic state d-orbital incomplete
• coloured complexes • variable oxidation state

Typical
• metals, hard, malleable, ductile
• High density
• High melting and B.P
• variable O.S
• complexes
• form alloy
• coloured compounds, catalyst

IB, IVB, VB, VIB, VIIB, VIIIB

Non-typical
• Doesn't follow the properties of transition elements
• kept in transition b/c
• variable O.S is not show
• Doesn't form coloured compound

• IIB, IIIB

Example
Sc → $4s^2 3d^1$

Binding energy
→ energy responsible for holding atoms together

B.E ∝ No. of unpaired e^-

⇒ mechanical properties of transition related to B.E e.g M.P and B.P

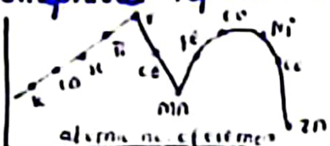
B.E ∝ strength of metallic bond → metallic bond due

• vanadium highest B.E

Left → right B.E increases but gradually de[creases] due to pairing

Fe^{+2} < Fe^{+3}
$4s^0 3d^6$ → 4 u.p
$4s^0 3d^5$ → 5 u.p
3d = dxy dyz dzx dx²-y² dz²

Graphical representation



Variable oxidation state
• Apparent charge on an atom (+) and (-ve)
• Transition elements are electropositive
• variable O.S , s and d less energy gap

Variable O.S ∝ No. of unpaired e^-

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$
+2, +3	+2, +3, +4								

+2, +3 | +2, +3, +4 | +2, +3, +4, +5 | +2, +3, +4, +5, +6

Catalytic Activity
: transition elements and compound are used as catalyst in O.C

Ni, Pd, Pt, $TiCl_4$ → variable O.S, they form intermediate and converted into product

SO_2, V_2O_5 → SO_3

Magnetic Behaviour

Paramagnetic
attraction in magnetic field due to unpaired e^-
e.g V, Cr, Mn

Diamagnetic
repelled due to paired e^-
e.g Zn, Cd, Hg

Ferromagnetic
can be magnetised
e.g Fe, Co, Ni

$\mu = \sqrt{n(n+2)}$ → unpaired e^-, Bohr magneton

Coordination compound
→ complex compound

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{-4}$ independent existence

G.F of complex compound :- $[ML_n]^k$ → metal atom, → charge, → Ligand, → coordination no., coordination sphere

Components

Metal atom or ion
surrounded by no. of ligands
Ex $K_4[Fe(CN)_6]$ $Cu(NH_3)_4]SO_4$
$Pt(Cl)(NO_2)(NH_3)_4]SO_4$

Ligand
• donated e^- pair
• coordinate covalent bond b/w metal and ligand
• monodentate : donate $1e^-$ [pair]
Cl^-, CN^-, OH^- → negatively
NH_3, CO, H_2O → Neutral
• Bidentate : donate $2e^-$ pair
CO_3^{-2}, SO_4^{-2}, $C_2O_4^{-2}$, en
Tridentate : Donate [illegible] [illegible]
Hexadentate: donate 6e pair
[illegible]

Coordination sphere Number
No. of e^- donated by ligand to central metal atom or ion
$K_4[Fe(CN)_6]$ → C.N
$[Pt(C_2O_4)_2]$
2×2 = 4
C.N

Charge on coordination sphere
central metal atom along with ligand placed in square bracket

Cationic: $[Cu(NH_3)_4]^{+2} SO_4^{-2}$
Anionic
Neutral: $[Ni(CO)_4]$

Nomenclature of complex compound

Rule: ① cation are named first than anion
$K_4[Fe(CN)_6]^{-4}$ Potassium

② Ligand (-ve) end 'o'

F^- Cl^- Br^- I^- CN^- $HCOO^-$ $C_2O_4^{-2}$
↓ ↓ ↓ ↓ ↓ ↓ ↓
Fluoro Chloro Bromo Iodo Cyano Aceto oxalato

③ Neutral H_2O NH_3 CO NO NH_2NH_2
Aqua Ammine carbonyl Nitrosyl hydrazine

④ Ligand → Alphabetically prefix → di, tri, tetra etc

⑤ Complex ion → -ve charge $[M]^{-ve}$ (L → Ligand, M → metal, R → Remain)
Name of metal atom end ate

⑥ oxidation no of metal ion is written in roman numerical parenthesis

⑦ Polydentate ligand
Bi → 2 → bidentate
Tri → 3 → tridentate

Chemistry of Chromium

• shinning, metallic, corrosion resistant element

oxidation

Oxidation of $Cr^{+3} \longrightarrow Cr^{+6}$

$[Cr(H_2O)_6]^{+3} + 3OH^- \xrightarrow[NaOH\ drop]{few} [Cr(H_2O)_3(OH)_3] + 3H_2O$
↓ Triaquatrihydroxo chromium III
Hexaquachromium II ion
Green solution Green ppt

$[Cr(H_2O)_3(OH)_3] + 3OH \xrightarrow[NaOH]{excess} [Cr(OH)_6]^{-3} + 3H_2O$
Green ppt hexa hydroxochromate VI ion
Green solution

$2[Cr(OH)_6]^{-3} + 3H_2O_2 \longrightarrow 2CrO_4^{-2} + 8H_2O + 2OH^-$
Green solution Bright yellow solution
hexahydroxochromate VI ion chromate ion.

Chromate and dichromate

• soluble in water, give yellow solution
• when acid is added to chromate VI CrO_4^{-2} ion an equilibrium is established and dichromate $Cr_2O_7^{-2}$ ion is formed

$2CrO_4^{-2} + 2H^+ \longrightarrow Cr_2O_7^{-2} + H_2O$
Yellow orange

$Cr_2O_7^{-2} + 2OH^- \longrightarrow 2CrO_4^{-2} + H_2O$
orange yellow.

Rxn with Zn: $K_2CrO_4 + 2Zn^{+2} + H_2O \rightarrow Zn(OH)_2$ (zincate ion) $+ 2K^+$

Rxn with Acid: $2K_2CrO_4 + 3H_2SO_4 \rightarrow 2K_2SO_4 + Cr_2(SO_4)_3 + 3H_2O + 3[O]$

KMnO4 as oxidizing agent

$K_2Cr_2O_7 + H_2SO_4 + FeSO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + Fe_2(SO_4)_3$

$K_2Cr_2O_7 + H_2SO_4 + (NH_4)_2SO_4FeSO_4 \cdot 6H_2O \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O +$

$K_2Cr_2O_7$ o.g in o.c

$CH_3-CH_3 + [O] \xrightarrow{K_2Cr_2O_7} CH_3-C(=O)-H + H_2O$ $(NH_4)_2SO_4 + Fe_2(SO_4)_3$

Shapes and colour of complexes

Coordination no. 2.

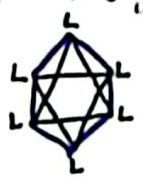
Linear shape
$L-M-L$ (180°)
Linear C.N = 2
Bond angle = 180°

Coordination no. 4

Tetrahedral → sp^3
square planer → dsp^2
$L-M-L$ (109.28°)
$[Zn(Cl_4)]^{-2}$

Coordination no. 6

Terms with prefix octahedral



octahedral

Colour of complexes

• All light absorb → Black colour
• All light reflect → white color
• Color emitted → color of compound

d-d splitting
transition metal bonded with ligand is splited into degenerate low and high energy level

d-d transition
↓
when light fall on transition complex having unpaired e energy absorbed excitation occ.

Chemistry of Maganese

Oxidation state: magnese have 7 different oxidation state

+1, +2, +3, +4, +5, +6, +7

=> stable ones are:- +7, +4, +2.

KMnO4 as oxidizing agent:

• strongest oxidizing agent

Basic medium
$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$
• MnO_4 is reduced from +7 to +6 state changing colour from purple / pink to Green solution

$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2[O]$
+7 → +4

Green solution → Brown solution

Acidic medium
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 5[O] + 3H_2O + 2MnSO_4$

KMnO4 as oxidizing agent in titration

Reaction with iron II sulphate:-
$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$

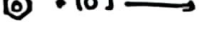
Reaction with oxalic acid. hot medium
$2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

Reaction with Mohr salt → double salt
$2KMnO_4 + 7H_2SO_4 + 10(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O \rightarrow K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 10(NH_4)_2SO_4 + 78H_2O$

Reaction with Na_2SO_3
$KMnO_4 + H_2SO_4 + Na_2SO_3 \rightarrow K_2SO_4 + MnSO_4 + H_2O + Na_2SO_4$

KMnO4 as o.g in organic chemistry.

Reaction with alkene (Baeyers reagent)
$CH_2=CH_2 + H_2O + [O] \xrightarrow[cold]{KMnO_4} CH_2(OH)-CH_2(OH)$ ethylene glycol

Reaction with alkyl benzene.


Chemistry of Iron

oxidation state:-

Fe^{+2} ; Fe^{+3}

↓ Ferrous — Green colour — unstable

↓ Ferric — yellow colour — stable

- Fe^{+2} → good reducing agent
- Fe^{+3} → oxidizing agent

$Fe^{+2} \longrightarrow Fe^{+3} + e^-$

Catalytic property:-

Iron acts as a catalyst

$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$

↓ comes from air by fractional distillation of liquid air

→ obtain by methane by reacting with steam

$S_2O_8^{-2} + 2I^- \xrightarrow{Fe^{+2}} 2SO_4^{-2} + I_2^0$

- Hexa aqua iron II ion $[Fe(H_2O)_6]^{+2}$
- Hexa aqua iron III ion $[Fe(H_2O)_6]^{+3}$ = yellow colour

Reaction with hydroxide ion:-

$[Fe(H_2O)_6]^{+2} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$

$[Fe(H_2O)_6]^{+3} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$

yellow sol — red brown ppt

Reaction with Ammonia:- Base and ligand

$[Fe(H_2O)_6]^{+3} + 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$

Green sol — Green ppt

$[Fe(H_2O)_6]^{+3} + 3NH_3 \rightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$

yellow color — red-brown ppt

Reaction with CO_3^{-2}

$Fe^{+2} + CO_3^{-2} \rightarrow FeCO_3$

$[Fe(H_2O)_6]^{+2} + 2CO_3^{-2} \rightarrow [Fe(H_2O)_4(OH)_2] + 2HCO_3^- + H_2O$

Reaction with thiocyanate ion:- CT for Fe^{+3}

$[Fe(H_2O)_6]^{+3} + SCN^- \rightarrow [Fe(H_2O)_5SCN]^{+2} + H_2O$

(Yellow solution) — Blood red (Pseudo aqueous ferric thiocyanate)

Chemistry of vanadium

- Silvery white metallic element

oxidation state:-

It has 7 different oxidation state

-1, 0, +1, +2, +3, +4, +5

- Lower oxidation state are unstable and act as reducing agent (-1 to +2)
- The most stable one are +4, +5

$V(-1) = [V(CO)_6]^{-1}$; $V(+3) = V_2O_3$

$V(0) = [V(CO)_6]$; $V(+4) = VOSO_4$

$V(+1) = V_2O$; $V(+5) = V_2O_5$

$V(+2) = VO$

Physical state and dissociation of V_2O_5

Yellow red poisonous solid

- melting point = 670°C
- slightly soluble in H_2O

$2VOSO_4 \rightleftharpoons 2VOSO_4 + O_2$

Chemistry of copper

oxidation state:- (exist in two oxidation)

Cu^{+1} ; Cu^{+2}

↓ cuprous, colourless compound in hydration (paramagnetic)

colourless

diamagnetic

→ $CuSO_4 \cdot 5H_2O$ → one coloured while cupric anhydrous are colourless

- $Cu^{+2} + H_2O \rightarrow [Cu(OH)]^+ + H^+$

Acidic — weakly acidic

- $[Cu(H_2O)_4]^{+2}$; $[Cu(H_2O)_6]^{+2}$

tetraaqua copper I ion colorless — blue — hexaaqua copper II ion blue solution

Reaction of hexaaqua copper II ion

$[Cu(H_2O)_6]^{+2} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$

Blue solution — Blue ppt

- Reaction with Ammonia:-

$[Cu(H_2O)_6]^{+2} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$

base — Blue ppt

$[Cu(H_2O)_6]^{+2} + 4NH_3 \rightarrow [Cu(H_2O)_2(NH_3)_4]^{+2} + 4H_2O$

deep blue sol — tetra amine di aqua copper II ion.

- Reaction with carbonate ions:-

$Cu^{+2} + CO_3^{-2} \longrightarrow CuCO_3$

(Blue solution) — Blue ppt

Color of complex

$VO_2^+ \xrightarrow{Zn/HCl} VO^{+2} \rightarrow [V(H_2O)_6]^{+3}$

yellow +5 — Blue +4 — Green +3

$[V(H_2O)_6]^{+3} \xrightarrow{Zn/HCl} [V(H_2O)_6]^{+2}$

Green — Purple.

Vanadium as an oxidizing agent

Rxn with HCl

→ oxidize HCl into Cl_2 which.

$V_2O_5 + 6HCl \rightarrow 2VOCl_2 + 3H_2O + Cl_2^0$

Rxn with nitric Acid.

$V_2O_5 + 2HNO_3 \rightarrow 2HVO_3 + N_2O_5$

Rxn with O_2 as catalyst.

- V_2O_5 is used in contact process
- sulphur dioxide to trioxide

$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$

Mechanism:

$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

$V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$

$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$

→ it is used because of its variable